

FORM PTO-1390

U.S. DEPARTMENT OF COMMERCE PATENT AND TRADEMARK OFFICE

**TRANSMITTAL LETTER TO THE UNITED STATES
DESIGNATED/ELECTED OFFICE (DO/EO/US)
CONCERNING A FILING UNDER 35 U.S.C. 371**

ATTORNEY DOCKET NUMBER IN-5453	U.S. APPLICATION NO. (IF KNOWN SEE 37 RR 15)	09/762030
INTERNATIONAL APPLICATION NO. PCT/EP 99/05180	INTERNATIONAL FILING DATE 21 July 1999 (21.07.99)	PRIORITY DATE CLAIMED 04 August 1998 (04.08.98)

TITLE OF INVENTION: **FILM AND THE USE THEREOF FOR COATING SHAPED PARTS**APPLICATION(S) FOR DO/EO/US: **HINTZE-BRÜNING, Horst; LASSMANN, Walter; STEGEMANN, Klaus; BLUM, Rainer; ANTONIETTI, Markus**

Applicant herewith submits to the United States Designated/Elected Office (DO/EO/US) the following items and other information:

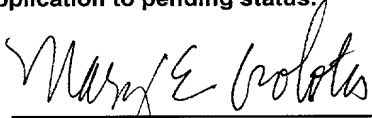
1. ☒ This is a FIRST submission of items concerning a filing under 35 U.S.C. 371.
2. ☐ This is a SECOND or SUBSEQUENT submission of items concerning a filing under 35 U.S.C. 371.
3. ☐ This express request to begin national examination procedures (35 U.S.C. 371(f)) at any time rather than delay examination until the expiration of the applicable time limit set in 35 U.S.C. 371 (b) and PCT Articles 22 and 39(1).
4. ☐ A proper Demand for International Preliminary Examination was made by the 19th month from the earliest claimed priority date
5. ☒ A copy of the International Application as filed (35 U.S.C. 371(c)(2))
 - a. ☐ are transmitted herewith (required only if not transmittal by the International Bureau).
 - b. ☒ have been transmitted by the International Bureau.
 - c. ☐ is not required, as the application was filed in the United States Receiving Office (RO/US)
6. ☒ A translation of the International Application into English (35 U.S.C. 371(C)(2)).
7. ☒ Amendment to the claims of the International Application under PCT Article 19 (35 U.S.C.371(c)(3))
 - a. ☐ are transmitted herewith (required only if not transmitted by the International Bureau).
 - b. ☐ have been transmitted by the International Bureau.
 - c. ☐ have not been made; however, the time limit for making such amendments has NOT expired.
 - d. ☒ have not been made and will not be made
8. ☐ A translation of the amendments to the claims under PCT Article 19 (35 U.S.C. 371(c)(3)).
9. ☐ An oath or declaration of the inventor(s) (35 U.S.C. 371(c)(4)).
10. ☐ A translation of the annex to the International Preliminary Examination Report under PCT Article 36

Items 11. to 16. below concern other document(s) or information included:

11. ☒ An Information Disclosure Statement under 37 CFR 1.97 and 1.98.
12. ☐ An assignment document for recording. A separate cover sheet in compliance with 37 CFR 3.28 and 3.31 is included
13. ☒ A FIRST preliminary amendment.
☐ A SECOND or SUBSEQUENT preliminary amendment.
14. ☐ A substitute specification.
15. ☐ A Change of power of attorney and/or address letter.
16. ☒ Other items or information:
A copy of the cover sheet from the PCT Published Application

I hereby certify that the attached correspondence is being deposited with the United States Postal Service in an envelope as "Express Mail Post Office to Addressee" Mailing Label No. **EK894924865US** addressed to the Assistant Commissioner for Patents, Washington, D.C. 20231 on **January 30, 2001.**


Marjorie Ellis

U.S. APPLICATION NO. (If known see 37 C.F.R. 1.50) 09/762030		INTERNATIONAL APPLICATION NO. PCT/EP 99/05180		ATTORNEY'S DOCKET NUMBER IN-5453	
17. <input checked="" type="checkbox"/> The following fees are submitted				CALCULATIONS PTO USE ONLY	
Basic National Fee (37 CFR 1.492(a)(1)-(5)): Neither international preliminary examination fee (37 CFR 1.482) Nor international search fee (37 CFR 1.445(a)(2)) paid to USPTO and International Search Report not prepared by the EPO or JPO..... \$970.00 International preliminary examination fee (37 CFR 1.482) not paid to USPTO but International Search Report prepared by the EPO or JPO..... \$860.00 International preliminary examination fee (37 CFR 1.482) not paid to USPTO but international search fee (37 CFR 1.44(a)(2)) paid to USPTO..... \$690.00 International preliminary examination fee (37 CFR 1.482) paid to USPTO but all claims did not satisfy provisions of PCT Article 33(1)-(4)..... \$670.00 International preliminary examination fee (37 CFR 1.482) paid to USPTO and all claims satisfied provisions of PCT Article 33(1)-(4) \$ 96.00					
ENTER APPROPRIATE BASIC FEE AMOUNT =				\$860.00	
Surcharge of \$130.00 for furnishing the oath or declaration later than <input type="checkbox"/> 20 <input type="checkbox"/> 30 months from the earliest claimed priority date (37 CFR 1.492(e)).				\$130.00	
Claims	Number Filed	Number Extra	Rate		
Total Claims	17 - 20 =	0	X \$18.00		
Independent claims	01- 03 =		X \$80.00	\$	
Multiple dependent claims(s) (if applicable)			+ \$260.00	\$	
TOTAL OF ABOVE CALCULATION =				\$990.00	
Reduction by 1/2 for filing by small entity, if applicable. Verified Small Entity statement must also be filed. (Note 37 CFR 1.9, 1.27, 1.28).				\$	
SUBTOTAL =				\$990.00	
Processing fee of \$130.00 for furnishing the English translation later the <input type="checkbox"/> 20 <input type="checkbox"/> 30 months from the earliest claimed priority date (37 CFR 1.492(f)).				\$	
TOTAL NATIONAL FEE =				\$990.00	
Fee for recording the enclosed assignment (37 CFR 1.21(h)). The assignment must be accompanied by an appropriate cover sheet (37 CFR 3.28, 3.31). \$40.00 per property +				\$	
TOTAL FEES ENCLOSED =				\$990.00	
				Amount to be:	
				refunded	
				Charged	
				\$990.00	
a. <input type="checkbox"/> A check in the amount of \$ _____ to cover the above fees is enclosed. b. <input checked="" type="checkbox"/> Please charge my Deposit Account No. <u>23-3425</u> in the amount of <u>\$990.00</u> to cover the above fees A triplicate copy of this sheet is enclosed. c. <input checked="" type="checkbox"/> The Commissioner is hereby authorized to charge any additional fees which may be required, or credit any overpayment to Deposit Account No. <u>23-3425</u> . A triplicate copy of this sheet is enclosed. NOTE: Where an appropriate time limit under 37 CFR 1.495 has not been met, a petition to revive (37 CFR 1.137(a) or (b)) must be filed and granted to restore the application to pending status.					
SEND ALL CORRESPONDENCE TO: BASF CORPORATION Patent Department 26701 Telegraph Road Southfield, Michigan 48034-2442 (248) 948-2020			 SIGNATURE Mary E. Golota Name 36,814 REGISTRATION NUMBER		

09/762030

PATENT

JC07 Rec'd PCT/PTO 3 1 JAN 2001
(Practitioner's Docket No. IN- 5453)

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re Application of

HINTZE-BRÜNING, Horst
LASSMANN, Walter
STEGEMANN, Klaus
BLUM, Rainer
ANTONIETTI, Markus

Serial No.: This application is a
National Phase of Patent Application
PCT/EP 99/05180 filed July 21, 1999.

Filed: January 26, 2001

For: FILM AND THE USE THEREOF
FOR COATING SHAPED PARTS

Group Art Unit: Not Assigned

Examiner: Not Assigned

I hereby certify that the attached correspondence is being deposited
with the United States Postal Service in an envelope as "Express Mail
Post Office to Addressee" Mailing Label No. **EK894924865**
addressed to the Assistant Commissioner for Patents, Washington,
D.C. 20231 on **January 30, 2001.**


Marjorie Ellis

PRELIMINARY AMENDMENT UNDER 37 CFR § 1.111

Hon. Commissioner of Patents and Trademarks
Washington, D.C.

Sir:

This preliminary amendment is submitted with the application for
entry into the U.S. National Phase under Chapter II. This application is
based on PCT/EP99/05180 filed July 21, 1999.

In connection with the filing of this National Phase application, please
make the following preliminary amendments.

09/762030

IN THE SPECIFICATION:

Please delete the titles "FILM AND ITS USE TO COAT MOLDINGS" and substitute therefor --FILM AND THE USE THEREOF FOR COATING SHAPED PARTS--.

On page 1, line 1, please insert -- This application claims priority under 35 U.S.C. Sec. 120 upon International PCT Application PCT/EP99/05180 and German Patent Application DE 198 35 193.3, filed August 4, 1998.--.

IN THE CLAIMS:

1. (Amended) A film comprising at least one support layer and [at least] one or more coating layers [applied thereon], wherein [there is] at least one of the one or more coating layers comprises a thermally curable [layer based on a] powder coating [material] or a thermally curable powder coating dispersion.

2. (Amended) The film [as claimed in] of claim 1, wherein at least one member selected from the group consisting of the thermally curable powder coating, [material or the] the thermally curable powder coating dispersion, and a polymer [of] in the powder coating [material] or [of] the powder coating dispersion, has a melting point of from 50 to 150°C[, preferably from 70 to 100°C].

3. (Amended) The film [as claimed in either] of claim[s] 1 [and 2], wherein the thermally curable powder coating [material] or the thermally

00752030-030204
FOOED-00029200

[illegible]

4.(Amended) The film [as claimed in any] of claim[s] 1[to 3],
[comprising at least one layer based on]wherein at least one of the one or
more coating layers results from the application of a liquid coating
material].

5. (Amended) The film [as claimed in any] of claim[s] 1 [to 4], wherein the support layer to be coated with the one or more coating [materials]layers is selected from the group consisting of a plastic, [preferably a thermoplastic, or] a self-supporting paint film, and mixtures thereof.

6. (Amended) The film [as claimed in any] of claim[s] 1[to 5], wherein at least one of the one or more coating layers compris[ing]es[at least one layer of] a surfacer composition.

7. (Amended) The film [as claimed in any] of claim[s] 1[to 6], wherein a removable film has been applied to the at least one coating layer [based on]comprising a thermally curable powder coating [material] or a thermally curable powder coating dispersion.

8.(Amended) The film [as claimed in any] of claim[s] 1[to 7], wherein

- the support layer has a thickness of from 10 to 1 000 μm , [preferably from 10 to 500 μm],

9. (Amended) A process for producing a coated film [as claimed in any] of claim[s] 1 [to 8], [which comprises]comprising

applying a thermally curable powder coating [material] or a thermally curable powder coating dispersion to [the]asupport layer or to [the]one or more layers [based on]comprising a liquid coating [material],

partially sintering the thermally curable powder coating [material] or drying the thermally curable powder coating dispersion, and, if desired, applying a removable film.

10. (Amended) A molding coated with a film [as claimed in any] of claim[s] 1[to 8].

11. (Amended) A method of coating moldings, [which comprises]comprising

applying a film [as claimed in any] of claim[s] 1[to 8] and [then]
crosslinking the at least one layer [based]comprising[on] the
thermally curable powder coating [material] or the thermally curable powder
coating dispersion[, the crosslinking taking place preferably by means of
heat supply or radiation].

12. (Amended) The use of a film as claimed in [any of] claim[s] 1[to 8] to coat moldings[, preferably vehicle bodies and domestic appliances].

13. (New) The film of claim 2, wherein at least one member selected from the group consisting of the thermally curable powder coating, the thermally curable powder coating dispersion, and a polymer in the powder coating or the powder coating dispersion, has a melting point of from 70 to 100°C.

14. (New) The film of claim 5, wherein the support layer to be coated with the one or more coating layers is a thermoplastic.

15.(New) The film of claim 8, wherein

- the support layer has a thickness of from 10 to 500 μm ,
- the layer based on a liquid coating material has a thickness of from 50 to 100 μm , and
- the at least one coating layer comprising a thermally curable powder coating or a thermally curable powder coating dispersion has a thickness of from 50 to 100 μm .

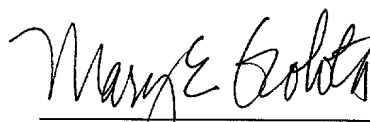
16. (New) The method of claim 11 wherein crosslinking occurs by means of heat supply or radiation.

17.(New) The use of a film as claimed in claim 1 to coat vehicle bodies and domestic appliances.

REMARKS

Upon entry of the present amendment claims 1- 17 will be pending in the application. Claims 1-12 have been amended in accordance with the requirements of U.S. patent practice. New claims 13-17 add no new matter, as these claims contain subject matter deleted from one or more of claims 1-12. Applicants respectfully request entry of the preliminary amendment.

Respectfully Submitted,



Mary E. Golota

Registration No. 36,814

Date: January 30, 2001
BASF Corporation
26701 Telegraph Road
Southfield, Michigan 48034-2442
(248)-948-2020

09763030-03034

Film and its use to coat moldings

The present invention relates to a film having at least one support layer and at least one coating
5 layer.

The use of films to coat exterior automobile parts is of increasing interest owing in particular to progress in thermoforming and in the technology of the "in-mold decoration" of polymer moldings (E. Bürkle in
10 Kunststoffe 87 (1997), 320-328; Modern Plastics International 11 (1997), 33-34; G. Steinbichler and J. Gießauf in Kunststoffe 87 (1997), 1262-1270).

State of the art are multilayer films whose transparent layer comprises thermoplastic polymers,
15 e.g., polyvinylidene fluoride (PVdF). Such films are available commercially, for example, as "in-mold surfacing film" from 3M/REXAM. WO 94/09983 and EP 361823 (AVERY DENNISON Corp.) describe multilayer films whose transparent layers comprise
20 PVdF/polyacrylate blends and whose pigmented color layers based on PVdF or polyvinyl chloride are applied thereto directly or via a tie layer. Via an adhesive layer, these assemblies are applied to the molding to be provided with the film, after an optional support
25 layer has been removed beforehand. Disadvantages of these films are the high halogen content of about 60% by weight (ecology and price) and also the inadequate service properties of the very soft transparent layers.

Furthermore, lacking sufficient extrudability, the PVdF-based layers are preferably applied from organic solution, necessitating a predetermined coating sequence of 1. transparent layer, 2. base layer, in
5 order to prevent bleeding phenomena in the bottom, effect layer, which is applied first, which would otherwise cause changes in shade and effect. Also known are transparent layers of thermoplastic polymethyl methacrylate (PMMA), obtained preferably by coextrusion
10 with the support layer and/or base layer (A. Grefenstein in Kunststoffe 87 (1997), 1332-1343). However, because of the high glass transition temperature, these layers tend toward brittleness and/or require narrow processing windows for the
15 deformation and handling of the films. Moreover, certain service properties of such layers do not meet the requirements imposed on high-grade transparent layers.

EP 251 546 describes a process for coating
20 automobile parts with a coated film. The film comprises a colored coating material which has been cured thermally beforehand. In EP 361 351 this process is implemented with radiation-curable coating materials, in order not to deform the thermoplastic support films
25 as a result of high temperatures.

The technical problem is to combine the film properties in the initial state (on the roll - nonflowing, nontacky, free from blocking) with the necessary thermoformability of the film during

5 literature describes approaches which produce and process films possessing latent curability in usually one layer, and in which the film, following its application, is cured to completion.

10 possess latent heat curability and are flowable in the melt, these films being used to seal metallic joints in automobile construction. On heating, the bottom layer expands and the top layer flows and, after curing, encloses the bottom layer.

15 The document DE 196 33 959 describes a process
of radiation-induced curing of a protective layer which
beforehand, as the outer layer of a preformed,
multilayer decorative film, has been backsprayed in the
injection mold with a thermoplastic. The resin
20 composition of the protective layer in the uncured
state comprises an acrylic copolymer main chain having
a glass transition temperature of from 40 to 120°C and
an average molecular weight (Mw) of preferably from
45 000 to 80 000 and also at least one (meth)acryloyl-
25 functional side chain which is provided with an at
least trifunctional crosslinker, containing (meth)-
acryloyl groups, and a photoinitiator.

As a result of the high glass transition point and the comparatively low functionality of (meth)acryloyl

groups of the polymer in the protective layer, the service properties of the films obtained following inventive irradiation of the applied decorative film are inadequate for the stringent requirements imposed on exterior automobile parts. Moreover, because of the high molecular weights of the main polymer, application can be made only from organic solution. Furthermore, the high expectations which exist in automobile construction cannot be met with the single-layer solutions proposed in the document.

The documents DE 196 54 918 A1 and DE 196 28 966 C1 (DAIMLER BENZ) propose partially curing a coating film on the film composite, which is then to be processed (i.e., rolled up) with a glass transition temperature of less than 40°C, in particular less than 30°C, without adhesion and can be thermoformed at temperatures slightly above the glass transition point. The finished part with the aforementioned layer, which has thus then been provided with a film, is subsequently subjected to final curing with electromagnetic radiation in order to ensure the service properties. Materials proposed and claimed for the exterior layer (i.e., transparent layer) applied and processed in this way include phosphazines, polyacrylates and polyurethanes as polymeric "binders". A disadvantage which may be mentioned for the solution described is that the uncured or part-cured film is intended to represent a continuous layer whose glass transition temperature is intended to lie within a

certain, very low temperature range in order to ensure simultaneously blocking resistance (absence of adhesion) and thermoformability (formability). Accordingly, the solution represents a classic
5 compromise between contradictory physical requirements (absence of adhesion, and stretchability). The degrees of freedom in the selection of suitable materials are therefore very low.

For the lamination of exterior automobile parts
10 there is therefore a need for multilayer films which as far as possible can be produced without solvent and without using halogenated thermoplastic polymers, which can be stored as blocking-resistant, nonflowing, windable stock, which during processing can be
15 thermoformed to give formings and which during or after application to the workpiece - either by vacuum-assisted lamination or by backspraying with thermoplastics in a mold - can be crosslinked to give smoothly leveled films, and whose appearance (shade and
20 effect range of the known automotive OEM coating materials) and service properties meet the present requirements of the automobile industry as regards OEM coating systems.

It is an object of the present invention,
25 therefore, to provide a film composite comprising a support layer and at least one coating layer applied thereon, which no longer has the problems indicated.

This object is achieved by the presence of at least one coating layer which is based on a powder coating material or on a powder coating dispersion.

In accordance with the invention, the layer
5 based on the powder coating material or the powder
coating dispersion may be applied directly to the
support layer. Preferably, a layer based on a liquid
coating material is applied, on to which the powder
coating material or the powder coating dispersion is
10 coated. Additionally, a surface layer and also a
removable cover film may be present. Accordingly, the
invention may result in a film composite comprising a
support film layer, an optional surfacer, an optional
liquid coating, a layer based on a powder coating
15 material or a powder coating dispersion, and an
optional transparent polymer film.

For example, the following variants may also be considered:

1. Optional adhesive layer, support film layer,
20 optional surfacer (primer), pigmented liquid
coating layer, powder clearcoat layer, optional
removable film.
2. Removable film, powder clearcoat layer, pigmented
liquid coating layer, optional surfacer (primer)
25 and/or adhesive, optional removable film.

Suitable materials for the layer based on a powder coating material are in principle all organic polymers known from paint chemistry. The selection is guided by the requirements specific to the application.

examples being the weather resistance and UV stability, intrinsic color, etc. Material to the invention are the requirements relating to the melting characteristics of the particles and to the ability for chemical, substantially emission-free crosslinking in the melt. Preferably, powder coating materials and aqueous suspensions of polymer powders are produced and processed in accordance with known processes.

A powder coating material which can be used in accordance with the invention may comprise, for example:

- a) at least one epoxide-containing binder containing from 20 to 45% of glycidyl-containing monomers accompanied, if desired, by vinylaromatic compounds, preferably styrene,
- b) crosslinking agents,
- c) if desired, catalysts, auxiliaries, additives typical of powder clearcoat materials, such as devolatiliziers, leveling agents, UV absorbers, free-radical scavengers, antioxidants.

Preference is given in this context to the following proportions:

- a) 60-80 parts
- b) 15-30 parts
- c) 3-10 parts

Examples of a suitable epoxy-functional binder for the solid powder clearcoat material are polyacrylate resins containing epoxide groups, which are preparable by copolymerizing at least one

ethylenically unsaturated monomer containing at least one epoxide group in the molecule with at least one further ethylenically unsaturated monomer containing no epoxide group in the molecule, at least one of the
5 monomers being an ester of acrylic acid or methacrylic acid. Polyacrylate resins of this kind containing epoxide groups are known, for example, from EP-A-299 420, DE-B-22 14 650, DE-B-27 49 576, US-A-4,091,048 and US-A-3,781,379.

10 Examples of ethylenically unsaturated monomers which contain no epoxide group in the molecule are alkyl esters of acrylic and methacrylic acid which contain 1 to 20 carbon atoms in the alkyl radical, especially methyl acrylate, methyl methacrylate, ethyl
15 acrylate, ethyl methacrylate, butyl acrylate, butyl methacrylate, 2-ethylhexyl acrylate and 2-ethylhexyl methacrylate. Further examples of ethylenically unsaturated monomers which contain no epoxide groups in the molecule are acid amides, such as acrylamide and
20 methacrylamide, for example, vinylaromatic compounds, such as styrene, methylstyrene and vinyltoluene, nitriles, such as acrylonitrile and methacrylonitrile, vinyl halides and vinylidene halides, such as vinyl chloride and vinylidene fluoride, vinyl esters, such as
25 vinyl acetate, for example, and hydroxyl-containing monomers, such as hydroxyethyl acrylate and hydroxyethyl methacrylate, for example.

The epoxide-functional monomers used in the epoxide-functional binders are preferably glycidyl

acrylate, glycidyl methacrylate and allyl glycidyl ether.

The polyacrylate resin containing epoxide groups normally has an epoxide equivalent weight of
5 from 300 to 2 500, preferably from 420 to 700, a number-average molecular weight (determined by gel permeation chromatography using a polystyrene standard) of from 2 000 to 20 000, preferably from 3 000 to 10 000, and a glass transition temperature (Tg) of from
10 30 to 80, preferably from 40 to 70, with particular preference from 40 to 60°C (measured with the aid of Differential Scanning Calorimetry (DSC)). Very particular preference is given to approximately 50°C. It is also possible to employ two or more acrylate
15 resins.

The polyacrylate resin containing epoxide groups may be prepared by widely known methods, by addition polymerization.

Preference is given in accordance with the
20 invention to the methyl/butyl mixed esters. These have the advantage over straight methyl esters of better solubility in polymer melts, and also to butyl/ethylhexyl mixed esters. Preference is also given, in accordance with the invention, to the
25 straight butyl esters.

As crosslinkers, various blocked polyisocyanates may be suitable. It is also possible to employ amino resins, e.g., melamines.

In principle, any amino resin suitable for transparent topcoat materials, or a mixture of such amino resins, may be used.

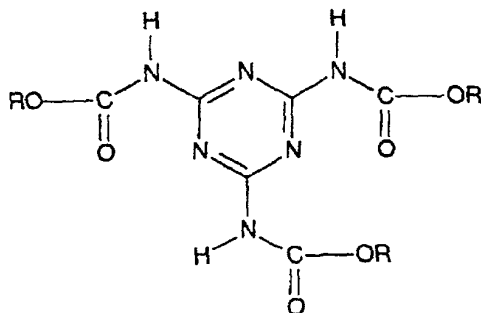
Resins of this kind are well known to the skilled worker and are offered by numerous companies as commercial products. Amino resins are condensation products of aldehydes, especially formaldehyde, and urea, melamine, guanamine and benzoguanamine, for example. The amino resins contain alcohol groups, preferably methylol groups, which in general are fully or partly etherified with alcohols.

Suitable further crosslinkers are carboxylic acids, especially saturated, straight-chain, aliphatic dicarboxylic acids having 3 to 20 carbon atoms in the molecule. Very particular preference is given to the use of dodecane-1,12-dioic acid. To modify the properties of the finished powder clearcoat materials it is possible, if desired, to use other carboxyl-containing crosslinkers. Examples that may be mentioned include saturated branched or unsaturated straight-chain dicarboxylic and polycarboxylic acids, and also polymers containing carboxyl groups.

Also suitable are powder clearcoat materials which comprise an epoxy-functional crosslinker and an acid-functional binder.

As component (b) it is also possible to use tris(alkoxycarbonylamino)triazines in accordance with US-A 4,939,213, US-A 5,084,541 and EP 0 624 577.

These are tris(alkoxycarbonylamino)triazines of the formula



where R = methyl, butyl, ethylhexyl groups. Derivatives
5 of these compounds may also be used.

The abovementioned crosslinking agents may also be used as a mixture of one or more of the abovementioned compounds. When making the selection it should, however, be ensured that no significant condensation products are formed during the subsequent thermal steps unless they are able to escape (e.g., in the injection mold or below a protective film).

Examples of suitable acid-functional binders are acidic polyacrylate resins which can be prepared by copolymerizing at least one ethylenically unsaturated monomer containing at least one acid group in the molecule with at least one further ethylenically unsaturated monomer containing no acid group in the molecule.

20 The binder containing epoxide groups and the crosslinker containing carboxyl groups, or, respectively, the carboxyl binder and epoxy crosslinker, are normally used in an amount such that there are from 0.5 to 1.5, preferably from 0.75 to

1.25, equivalents of carboxyl groups per equivalent of epoxide groups. The amount of carboxyl groups present can be determined by titration with an alcoholic KOH solution.

5 In accordance with the invention, the binder comprises vinylaromatic compounds, especially styrene. In order to limit the risk of cracking on weathering, however, the amount is not more than 35% by weight. From 10 to 25% by weight is preferred.

10 If desired, the solid powder coating materials comprise one or more suitable catalysts for the epoxy resin curing. Suitable catalysts are phosphonium salts of organic or inorganic acids, quaternary ammonium compounds, amines, imidazole and imidazole derivatives.

15 The catalysts are generally used in proportions of from 0.001% by weight to about 2% by weight, based on the overall weight of the epoxy resin and the crosslinking agent.

 Examples of suitable phosphonium catalysts are
20 ethyltriphenylphosphonium iodide, ethyltriphenylphosphonium chloride, ethyltriphenylphosphonium thiocyanate, ethyltriphenylphosphonium acetate-acetic acid complex, tetrabutylphosphonium iodide, tetrabutylphosphonium bromide and tetrabutylphosphonium acetate-
25 acetic acid complex. These and other suitable phosphonium catalysts are described, for example, in US-A 3,477,990 and US-A 3,341,580.

 Examples of suitable imidazole catalysts are 2-styrylimidazole, 1-benzyl-2-methylimidazole, 2-methyl-

imidazole and 2-butylimidazole. These and other imidazole catalysts are described, for example, in the Belgian patent no. 756,693.

Furthermore, the solid powder coating materials
5 may also, if desired, comprise auxiliaries and additives. Examples thereof are leveling agents, antioxidants, UV absorbers, free-radical scavengers, free-flow aids and devolatiliziers, such as benzoin, for example.

10 The solid powder coating materials are prepared in accordance with known methods (cf., e.g., product information bulletin from BASF Lacke + Farben AG, "Pulverlacke" [Powder coating materials], 1990) by homogenization and dispersion using, for example, an
15 extruder, screw kneading device and the like. Following preparation of the powder coating materials, they are prepared for dispersion by milling and, if appropriate, by classifying and sieving.

The powder clearcoat material may also be
20 present in the form of an aqueous dispersion. This dispersion preferably comprises a component A in the form of the solid powder coating material and an aqueous component B. Particular preference is given to an aqueous powder clear coat dispersion comprising
25 a solid, pulverulent component A and an aqueous component B, where

component A is a powder clearcoat material comprising
a) at least one epoxide-containing binder containing
from 20 to 45%, preferably from 25 to 35% of

glycidyl-containing monomers, accompanied if desired by vinylaromatic compounds, preferably styrene,

- b) crosslinking agents, and
- 5 c) if desired, catalysts, auxiliaries, additives typical of powder clearcoat materials, such as devolatiliziers, leveling agents, UV absorbers, free-radical scavengers, antioxidants and
- 10 component B is an aqueous dispersion comprising
 - a) at least one, preferably nonionic, thickener, and
 - b) if desired, catalysts, auxiliaries, defoamers, dispersing auxiliaries, wetting agents, preferably carboxy-functional dispersants, antioxidants, UV
 - 15 absorbers, free-radical scavengers, small amounts of solvent, leveling agents, biocides and/or water retention agents.

In accordance with the invention, preference is given to the following proportions for the components A and B:

Component A

- a) 60-80 parts
- b) 15-30 parts
- 25 c) 3-10 parts

Component B

- a) 20-50 parts of component A
- b) 80-50 parts of component B

c) 1'000-5 000 parts of distilled water

The dispersion contains preferably 25-100 parts of component A and 100 parts of component B.

5 Preference is given in accordance with the invention to nonionic associative thickeners a).

Structural features of such associative thickeners a) are:

10 aa) a hydrophilic framework, which ensures sufficient solubility in water, and

ab) hydrophobic groups, which are capable of associative interaction in the aqueous medium.

15 Examples of hydrophobic groups used are long-chain alkyl radicals, such as dodecyl, hexadecyl or octadecyl radicals, for example, or alkaryl radicals, such as octylphenyl or nonylphenyl radicals, for example.

20 Hydrophilic frameworks used are preferably polyacrylates, cellulose ethers or, with particular preference, polyurethanes, containing the hydrophobic groups as polymer building blocks.

Very particularly preferred hydrophilic frameworks are polyurethanes containing polyether chains as building blocks, preferably comprising polyethylene oxide.

25 In the synthesis of such polyether polyurethanes, the diisocyanates and/or polyisocyanates, preferably aliphatic diisocyanates, with particular preference unsubstituted or alkyl-substituted 1,6-hexamethylene diisocyanate, are used to link the hydroxyl-terminated

polyether building blocks with one another and to link the polyether building blocks with the hydrophobic end-group building blocks, which may, for example, be monofunctional alcohols and/or amines containing the
5 abovementioned long-chain alkyl radicals or aralkyl radicals.

The dispersing auxiliaries which may be used with preference in component B include polyurethanes.

These may preferably comprise

- 10 1. at least one organic component containing at least two reactive hydrogen atoms,
2. a monofunctional ether, and
3. a polyisocyanate.

The organic component of the polyurethane
15 composition comprises a polyester polyol, a low molecular mass diol and/or triol, or mixtures thereof. If desired, a trifunctional monomer containing hydroxyl groups may be used.

In a second preferred embodiment, the
20 polyurethane comprises

1. at least one organic component containing at least two reactive hydrogen atoms,
2. a nonionic stabilizer prepared by reacting
 - 25 i. a monofunctional polyether with a polyisocyanate component, in order to produce an isocyanate intermediate, and
 - ii. a component containing at least one active amine group and at least two active hydroxyl groups, and

3. at least one polyisocyanate component.

The organic component preferably comprises polyether polyester polyol, a low molecular mass diol and/or triol, or mixtures thereof.

5 The polyester component may be prepared by reacting at least one dicarboxylic acid and at least one alcohol component, the alcohol containing at least two hydroxyl groups. The carboxylic acid component contains two or more carboxyl groups.

10 In addition to the carboxylic acid, the polyester resin may also include one or more low molecular mass diols or triols. Any polyol may be used in principle.

The polyester resins or mixtures of polyester
15 resins that are used preferably contain terminal hydroxyl groups. This is brought about by adding an excess of polyols.

To synthesize the polyesters it is possible to use both monocarboxylic acids and monoalcohols.
20 Preferably, however, the monocarboxylic acids and/or monoalcohols are present in the polyester resin in a very low amount by weight.

The polyester diol components preferably used contain between 20 and 80% by weight of the
25 polyurethane resin. The amounts are preferably between 50 and 70% by weight. Very particular preference is given to from 55 to 65% by weight.

To prepare the polyurethane, polyester polyols having a molecular weight of between 500 and 5 000 are

used." Preference is given to molecular weights of between 1 000 and 3 500.

In addition to the polyester diols, the polyurethane resins may contain further organic components containing at least two reactive hydrogen atoms. These are preferably diols and triols, thiols and/or amines, or mixtures of these substances. The components used to synthesize the polyester component may also be employed as separate components in this case. In other words, dialcohols or trialcohols, such as neopentyl glycol or 1,6-hexanediol, for example, are also suitable as an additional organic component in the polyurethane.

The molecular weight of the diols and/or triols used in the polyurethane resin is between 0 and 20% by weight. From 1 to 6% by weight is preferred.

The polyurethane resin further comprises polyisocyanates, especially diisocyanates. The isocyanates are present at between 5 and 40% by weight, based on the polyurethane mass. Particular preference is given to from 10 to 30% by weight and very particular preference to from 10 to 20% by weight. To prepare the polyurethane, finally, a monofunctional polyether is used.

In a second variant, a nonionic stabilizer is prepared in which, preferably, a monofunctional polyether is reacted with a diisocyanate. The reaction product formed is then reacted with a component

containing at least one active amine group and at least two active hydroxyl groups.

In one particular embodiment, the polyurethane comprises a reaction product of:

- 5 1. a polyester polyol, in turn comprising a reaction product of a carboxylic acid containing at least two carboxyl groups and a component containing at least two hydroxyl groups,
2. at least one low molecular mass component
10 containing at least two hydroxyl groups,
3. at least one polyisocyanate component,
4. a nonionic stabilizer prepared by reacting a monofunctional ether with a polyisocyanate and then reacting the resulting reaction product with
15 a component containing at least one active amine and at least two active hydroxyl groups.

In a fourth variant, the polyurethane comprises a reaction product of

1. a polyester polyol,
- 20 2. at least one low molecular mass diol or triol,
3. a polyisocyanate,
4. a monomer containing trihydroxy groups,
5. a monofunctional hydroxyl-containing polyether.

The polyesters are synthesized with the above-
25 described carboxylic acid components and an excess of polyols. The excess of polyols is chosen so as to give, preferably, terminal hydroxyl groups. The polyols preferably have a hydroxyl functionality of at least two.

The polyester resin preferably comprises one or more polyols, preferably a diol. Diols used with preference are alkylene glycols, such as ethylene glycol, propylene glycol, butylene glycol and neopentyl glycol, 1,6-hexanediol or other glycols, such as bisphenol A, cyclohexanedimethanol, caprolactonediol, hydroxyalkylated bisphenol and similar compounds.

The low molecular mass diols that are preferably used in accordance with the invention are known from the prior art. They include aliphatic diols, preferably alkylene polyols having 2 to 18 carbon atoms. Examples thereof are 1,4-butanediol, cycloaliphatic diols, such as 1,2-cyclohexanediol and cyclohexanedimethanol.

Organic polyisocyanates suitable in accordance with the invention are preferably those containing at least two isocyanate groups. Particular preference is given to diisocyanates, e.g., p-phenylene diisocyanate, 4,4'-biphenyl diisocyanate, toluene diisocyanate, 3,3'-dimethyl-4,4'-biphenylene diisocyanate, 1,4-tetramethylene diisocyanate, 1,6-hexamethylene diisocyanate, 2,2,4-trimethylhexane 1,6-diisocyanate, methylenebis(phenyl isocyanates), 1,5-naphthalene diisocyanate, bis(isocyanatoethyl fumarate), isophorone diisocyanate and methylenebis(4-cyclohexyl isocyanate).

Besides the abovementioned diisocyanates, other polyfunctional isocyanates are also used. Examples are 1,2,4-benzene triisocyanate and polymethylene-polyphenyl isocyanates.

Particular preference is given to the use of aliphatic diisocyanates, e.g., 1,6-hexamethylene diisocyanate, 1,4-butylene diisocyanate, methylene-bis(4-cyclohexyl isocyanate), isophorone diisocyanate
5 and 2,4-toluene diisocyanate.

Longer-chain polyurethane resins may be obtained by chain extension with components containing diol and/or triol groups. Particular preference is given to chain extenders containing at least two active
10 hydrogen groups, examples being diols, thiols, diamines or mixtures of these substances, e.g., alkanolamines, aminoalkyl mercaptans, hydroxyalkyl mercaptans and similar compounds.

Examples of diols used as chain extenders are
15 1,6-hexanediol, cyclohexanedimethylol and 1,4-butane-diol. A particularly preferred diol is neopentyl glycol.

The polyethers which can be used are preferably monofunctional or difunctional polyethers. Examples of
20 the monofunctional ones include those prepared by polymerizing ethylene oxides, propylene oxides or mixtures thereof.

The polyurethane product described may be mixed with conventional crosslinkers. These include,
25 preferably, amino resins, e.g., melamine. It is also possible to use condensation products of other amines and amides, examples being aldehyde condensates of triazines, diazines, triazoles, guanidines, guanamines or alkyl- and aryl-substituted derivatives of such

components. Some examples of such components are N,N'-dimethylurea, dicyandiamides, 2-chloro-4,6-diamino-1,3,5-triazine, 6-methyl-2,4-diamino-1,3,5-triazine, 3,5-diaminotriazole, triaminopyrimidines, 2-mercapto-
5 4,6-diaminopyrimidine, 2,4,6-triethyltriamino-1,3,5-triazine and similar substances.

Suitable aldehydes are preferably formaldehyde. It is likewise possible to use acetaldehyde, crotonaldehyde, acrolein, benzaldehyde, furfural.

10 The amine-aldehyde condensation products may include methylol or similar alcohol groups. Examples of alcohols that can be used are methanol, ethanol, propanol, butanol, pentanol, hexanol, heptanol, benzyl alcohol and aromatic alcohols, cyclic alcohols, such as
15 cyclohexanol, monoethers or glycols, and also substituted alcohols, e.g., 3-chloropropanol.

In addition to the abovementioned isocyanates it is also possible to use blocked polyisocyanates as crosslinking agents. Examples of these include organic
20 polyisocyanates such as trimethylene, tetramethylene, hexamethylene, 1,2-propylene, 1,2-butylene and 2,3-butylene diisocyanates. Likewise suitable for use are cycloalkene components such as 1,3-cyclopentane, 1,4-cyclohexane and 1,2-cyclohexane diisocyanates. It
25 is also possible to use aromatic components such as phenylene, p-phenylene, 4,4'-biphenyl, 1,5-naphthalene and 1,4-naphthalene diisocyanates. Also suitable, furthermore, are aliphatic-aromatic components such as 4,4'-diphenylenemethane, 2,4- or 2,6-tolylene or

mixtures thereof, 4,4'-toluidine and 1,4-xylylene diisocyanates. Further examples are ring-substituted aromatic components such as 4,4'-diphenyl ether diisocyanates and chlorodiphenylene diisocyanates.

5 Triisocyanates which can be used are triphenylmethane 4,4'4''-triisocyanate, 1,3,5-triisocyanatobenzene and 2,4,6-triisocyanatotoluene. Tetraisocyanates which may be used, finally, include 4,4'-diphenyldimethylmethane 2,2',5,5'-tetraisocyanate.

10 Blocking agents which can be used include aliphatic, cycloaliphatic and aromatic alkyl monoalcohols. Examples include methyl, ethyl, chloroethyl, propyl, butyl, cyclohexyl, heptyl, octyl and nonyl alcohols, 3,3,5-trimethylhexanol, decyl
15 alcohol and lauryl alcohol. Examples of phenolic components which can be used are phenols or substituted phenols. Examples thereof are cresol, xylenol, nitrophenol, chlorophenol, ethylphenol, 1-butylphenol and 2,5-di-t-butyl-4-hydroxytoluene.

20 Further suitable blocking agents are tertiary hydroxylamines, e.g., diethylethanolamine and oximes, such as methyl ethyl ketone oxime, acetone oxime and cyclohexanone oxime.

The crosslinking agents described are present
25 in the polyurethane dispersion in amounts from 2 to 15% by weight, preferably from 4 to 8% by weight.

The polyurethane obtained may be present in the powder slurry with a proportion of from 2 to 20% by weight, preferably from 5 to 15% by weight.

The aqueous powder clearcoat dispersion may be prepared from the components A and B by wet milling or by stirred incorporation of dry-milled powder coating material. Particular preference is given to wet
5 milling.

Following the dispersion of component A in component B, milling is carried out if appropriate, the pH is adjusted to 4.0-7.0, preferably 5.5-6.5, and the dispersion is filtered.

10 The average particle size is between 1 and 25 μm , preferably less than 20 μm , with particular preference from 3 to 10 μm . The solids content of the aqueous powder clearcoat dispersion is between 15 and 50%.

15 Before or after the wet milling and/or the introduction of the dry powder coating material into the water, from 0 to 5% by weight of a defoamer mixture, an ammonium and/or alkali metal salt, a dispersing auxiliary, wetting agent and/or thickener
20 mixture, and also the other additives, may be added to the dispersion. In accordance with the invention, defoamers, dispersing auxiliaries, wetting agents and/or thickeners are preferably first dispersed in water. Then small portions of the powder clearcoat
25 material are stirred in. Subsequently, defoamers, dispersing auxiliaries, thickeners and wetting agents are again incorporated by dispersion. Finally, small portions of powder clearcoat materials are again stirred in.

In accordance with the invention, the adjustment of the pH is carried out preferably using ammonia or amines. In this case, the pH may initially rise, so that a strongly basic dispersion is formed.

5 However, over the course of several hours or days, the pH drops back to the values indicated above.

Another variant for preparing the powder clearcoat dispersion of the invention comprises mixing a liquid melt of the binders and crosslinkers and, if
10 desired, of the additives c) with component A, in an emulsifying apparatus, preferably with the addition of water and stabilizers, cooling the resulting emulsion and filtering it.

As material for the layer based on the liquid
15 coating material, which may be present, if desired, between film and powder coating layer, all coating systems currently in existence are suitable.

In particular, it is possible to use any basecoat material suitable for the conventional coating
20 of automobile bodies. A prerequisite, however, is good flexibility of the cured coating material, without any loss of resistance to stone chipping and corrosion. Coating materials of this kind are well known to the skilled worker. They essentially comprise a polymeric
25 binder, an optional crosslinking agent, and also a pigment or a mixture of pigments.

As its binder, the basecoat material which can be employed in accordance with the invention may comprise, for example, a polyester resin, a

polyurethane resin or a polyacrylate resin, or a mixture of such binders.

In particular, the liquid coating material may further comprise rheological agents and also other coating auxiliaries. It is of course also possible for pigments of any kind, examples being color pigments such as azo pigments, phthalocyanine pigments, carbonyl pigments, dioxazine pigments, titanium dioxide, pigmentary carbon black, iron oxides and chromium and/or cobalt oxides, or effect pigments such as metal flake pigments, especially aluminum flake pigments, and pearlescent pigments, to be incorporated, and/or liquid-crystalline polymers.

Furthermore, the liquid coating materials which can be employed may, if desired, comprise further customary auxiliaries, additives, suitable light stabilizers (e.g., HALS compounds, benzotriazoles, oxalanilide and the like), slip additives, polymerization inhibitors, flattening agents, defoamers, leveling agents and film-forming auxiliaries, e.g., cellulose derivatives, or other additives commonly employed in basecoat materials. These customary auxiliaries and/or additives are usually used in an amount of up to 15% by weight, preferably from 2 to 9% by weight, based on the weight of the coating material without pigments and without fillers.

Finally, the liquid coating material may also contain adhesion promoting agents, in order to improve the bond between films and powder coating material.

Particularly suitable for this purpose are functional silanes, (transition) metal complexes and their alkoxides, polyamines, halogenated and/or polar-modified polyolefins (e.g., in accordance with
5 EP 0 755 422), and amphiphilic block copolymers.

Here again, however, a prerequisite is good flexibility of the cured coating material without any loss of the resistance to stone chipping and corrosion. Coating materials of this kind are well known to the
10 skilled worker.

As crosslinking agent, the basecoat material may comprise an amino resin, a polyisocyanate resin, a carboxyl-containing crosslinking agent, or a mixture of such crosslinking agents.

15 Also suitable are tris(alkoxycarbonylamino)triazines. It is likewise possible to use derivatives thereof. With preference it is possible to use tris(alkoxycarbonylamino)triazines as are described in US-A 5084541.

20 The dry film thickness of the applied liquid coating film should be between 15 and 200 μm , preferably between 50 and 100 μm .

The dry film thickness of the applied film based on powder coating material or on powder coating
25 dispersions should be between 30 and 200 μm , preferably between 50 and 100 μm .

Where the film of the invention coated with the described coating materials is used for vehicle bodies and for that purpose is to be additionally coated with

a surfacer composition, it is possible with preference to use surfacer compositions suitable for coating automobile bodies. Here again, the flexibility must be sufficient for the purposes of the invention. In accordance with the invention, this flexibility can be controlled by way of the degree of crosslinking.

The surfacer coat obtained in this way has essentially three functions: firstly, it is intended to compensate for the unevennesses and secondly to improve the resistance of the overall coating system to stone chipping. Moreover, the surfacer serves to promote adhesion between film polymer and coating system. For this purpose, the surfacer may comprise the adhesion promoting agents mentioned in connection with the liquid coating material. The surfacer compositions may consist essentially of a binder, a crosslinking agent, pigments and fillers, and, if desired, further additives, such as crosslinking catalysts and leveling auxiliaries, for example.

As binders, the surfacer compositions which can be used may comprise epoxy resins, polyester resins, polyurethane resins, polyacrylate resins and alkyd resins, or combinations of such resins. As crosslinking agents, the surfacer compositions which may be used may comprise amino resins, such as for example, melamine-formaldehyde resins, amines, polyisocyanates and carboxyl-containing compounds. Examples of pigments which may be present in the surfacer compositions which may be used are titanium dioxide, phthalocyanines, iron

oxides and carbon black. As fillers, the surfacer compositions may for example comprise lime or barium sulfate.

Suitable materials for the support layer that
5 is to be coated include all thermoplastics such as
polyolefins, polyesters, polyamide, polyurethane,
polyacrylate, especially copolymers of acrylonitrile,
styrene, acrylic esters (e.g., grades of LURAN and
LURAN S.). Also suitable of course are blends of
10 different thermoplastics, for example, of polycarbonate
and polybutylene terephthalate. Likewise suitable are
mixtures of the aforementioned substances. The film
thickness may be between 10 and 1 000 μm , preferably
from 10 to 500 μm , most preferably from 20 to 250 μm ,
15 and is guided only by practical aspects for the
processing.

In addition to the abovementioned materials,
self-supporting paint films may also be used as the
support layer. Such paint films are described, for
20 example, in DE 195 35 934.

A transparent polymer film may be applied to
the layer based on the above-described powder coating
materials or powder coating dispersions. For this film
it is possible in principle to use the materials which
25 are also suitable for the support film. For reasons of
cost, polyolefin films are preferred.

The films coated in accordance with the
invention may be rolled up. Consequently, the products
may be offered and supplied in the form of rolls. For

this reason, the coating materials used in accordance with the invention must have a flexibility which is sufficient for rolling up.

In accordance with the invention it may be envisaged not to obtain a continuous film layer of the powder coating material or of the powder clearcoat dispersion in the unprocessed state of the film, but instead to apply a very close packing of material particles having average diameters of less than 50 μm , preferably less than 15 μm , with particular preference less than 10 μm , to the film or to a film provided with a pigmented layer based on a liquid coating material. The particles of material have preferably a melting point of from 50 to 150°C, preferably from 70 to 100°C and are sintered with one another (locally bonded at the points of contact) to such an extent that the coated film can be wound up without problems.

Accordingly, the powder coating dispersion or the powder coating material is preferably present in sintered, partially crosslinked form or - in the case of the powder coating dispersion - in dried form.

In processing, the film may be formed even at temperatures below the melting point of the particles. In this case, the particles bonded locally to one another may be separated at their contact points. In the case of local severe deformation, it is possible in this case for macroscopic, visually perceptible cracks to appear in the layer. Since in this state the material is still completely uncrosslinked, the cracks

may subsequently be closed by passing thermal energy through the flowing material (when the film is used to decorate thermoplastic parts, this takes place preferably in the injection mold as a result of the hot polymer mass). In this state, the final curing of the material may also then take place. Said final curing may take place optionally by a thermally (catalyzed or not) proceeding chemical crosslinking (preferably addition reactions without notable emissions of, for example, masking agents). The thermal crosslinking may preferably take place while still in the injection mold, and/or by the action of hot media (e.g., circulating air) on the molding already provided with the film. The result obtained comprises fully cured films having excellent appearance (surface smoothness, gloss) and very good service properties (corresponding to known OEM clearcoat technologies).

The films may in principle also be applied to all molding blanks, preferably metal panels, which are suitable for producing vehicle bodies, surface-mounted parts for vehicle bodies, domestic appliances, e.g., refrigerators, washing machines, dishwashers. Predominantly, the films are applied to pretreated metal panels. These panels may have been pretreated by phosphating and/or chromating, for example.

The coated films prepared as described above may be laminated on to the surface of a molding blank, i.e., of an as yet unformed substrate, preferably a metal panel. In this case, the film may first be

laminated on to the unformed substrate, followed by forming of the substrate, and finally by the formation of a film, and curing thereof.

Adhesion to the surface to be coated may be brought about in a variety of ways. One possibility, for example, is to use films which have adhesion promoting groups, such as urethane groups, acid anhydride groups or carboxyl groups, for example, or films which have been provided with adhesion promoting groups by coextrusion with a polymer containing adhesion promoting groups. The adhesion between the film and the surface that is to be coated may also be brought about by the use of an adhesive. In this case, use may be made both of adhesives which are solid at room temperature and of adhesives which are liquid at room temperature.

Implementation examples

1. Preparation of the acrylate resin

21.1 parts of xylene are introduced as an initial charge and this charge is heated to 130°C. The following are metered into the initial charge at 130°C over the course of 4 h by way of two separate feed vessels: initiator: 4.5 parts of TBPEH (tert-butyl perethylhexanoate) mixed with 4.86 parts of xylene, and monomers: 10.78 parts of methyl methacrylate, 25.5 parts of n-butyl

methacrylate, 17.39 parts of styene and 23.95 parts of glycidyl methacrylate. The mixture is subsequently heated to 180°C and the solvent is stripped off under reduced pressure < 100 mbar.

5

1.1. Preparation of the powder clearcoat material

77.5 parts of acrylate resin, 18.8 parts of dodecanedicarboxylic acid (acid curing agent), 2 parts of Tinuvin 1130 (UV absorber), 0.9 parts of Tinuvin 144 (HALS), 0.4 parts of Additol XL 490 (leveling agent) and 0.4 parts of benzoin (devolatilizer) are intimately mixed on a Henschel fluid mixer, the mixture is extruded on a BUSS PLK 46 extruder, the extrudate is ground on a Hosokawa ACM 2 mill, and the milled material is sieved off through a 125 µm sieve.

10
15

1.2. Preparation of the dispersion

20

0.6 parts of Troykyd D777 (defoamer), 0.6 parts of Orotan 731 K (dispersing auxiliary), 0.06 parts of Surfinol TMN 6 (wetting agent) and 16.5 parts of RM8 (Rohm & Haas, nonionic associative thickener based on polyurethane) are dispersed in 400 parts of deionized water. Then 94 parts of the powder clearcoat material are introduced in small portions, with stirring. Subsequently, a further 0.6 parts of Troykyd D777, 0.6 parts of Orotan 731

25

K, 0.06 parts of Surfinol TMN 6 and 16.5 parts of RM8 are incorporated by dispersion. Finally, 94 parts of the powder clearcoat material are introduced in small portions, with stirring. The material is milled in a sand mill for 3.5 h. The finally measured average particle size is 4 μm . The material is filtered through a 50 μm filter and, finally, 0.05% Byk 345 (leveling agent) is added.

10

1.3. Application of the dispersion

The slurry is applied by means of a gravity flow cup gun to steel panels coated with aqueous basecoat material. The metal sheet is flashed off at room temperature for 5 minutes and at 60°C for 5 minutes. Subsequently, the metal sheet is baked at a temperature of 140°C for 30 minutes.

At a film thickness of 40 μm , a high-gloss clearcoat film with MEK resistance (> 100 double strokes) is produced.

The condensation resistance of the clearcoat film is good.

2. Production of a film coated with clearcoat composition.

2.1 Film coated with polymer

5 A 400 μm thick film of acrylonitrile-styrene-acrylate copolymer (LURAN S 797, BASF AG) is rollercoated with a commercially customary aqueous basecoat material for automotive coatings and is dried by passing it through a segmented convection oven with heated air with a temperature gradient from 40 to 100°C and a residence time of two minutes so as to give a tack-free film without thermosetting crosslinking. The dry film thickness is 50 μm . The suspension obtained in 1.2 is applied by roller blade application to the basecoat thus obtained. The evaporation of the water and the pointwise binding of the dried polymer particles takes place during two-minute passage through a segmented convection oven whose air has a temperature gradient between 50 and 100°C. The result is a blocking-free, non-flowing film with a 70 μm thick, nontransparent, white clearcoat, which is windable and storable.

2.2 Forming and curing of the film

25 The film is bent around a cylinder by its uncoated side at room temperature. The formed film remains crack-free (cylinder diameter ≥ 10 cm) or exhibits increasingly macroscopic cracks in the white clearcoat (cylinder diameter < 10 cm). After

a period of 30 minutes in a forced air oven with hot air at 150°C, all of the cracks have flowed closed in each case, and a smoothly leveled, transparent clearcoat is obtained which has no defects, a high gloss (≥ 85 units at 20° observation angle) and low haze (≤ 30 units at 20° observation angle).

2.3 Service properties of the cured film

10

Exposure to gasoline at room temperature for 24 hours causes no change to the visual appearance of the film. Film constructions applied to steel plate exhibit resistance to tree resin, tar and one percent sulfuric acid of typically 38°C, 42°C and 40°C respectively (the gradient oven temperature at which markings become visible in the film). Storage for ten days at 40°C and 95% relative atmospheric humidity causes no visual change in the film, and no loss of adhesion following one-hour regeneration of the films in the ambient air.

15

20

What is claimed is:

1. A film comprising at least one support layer and at least one coating layer applied thereon, wherein
5 there is at least one thermally curable layer based on a powder coating material or a powder coating dispersion.
2. The film as claimed in claim 1, wherein the powder coating material or the polymer of the powder
10 coating material or of the powder coating dispersion has a melting point of from 50 to 150°C, preferably from 70 to 100°C.
3. The film as claimed in either of claims 1 and 2, wherein the powder coating material or the powder
15 coating dispersion is present in the form of a sintered, partially crosslinked and/or dried layer.
4. The film as claimed in any of claims 1 to 3, comprising at least one layer based on a liquid coating material.
- 20 5. The film as claimed in any of claims 1 to 4, wherein the support layer to be coated with the coating materials is a plastic, preferably a thermoplastic, or a self-supporting paint film.
6. The film as claimed in any of claims 1 to 5,
25 comprising at least one layer of a surfacer composition.
7. The film as claimed in any of claims 1 to 6, wherein a removable film has been applied to the layer

based on a powder coating material or a powder coating dispersion.

8. The film as claimed in any of claims 1 to 7, wherein

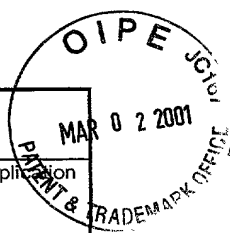
- 5 - the support layer has a thickness of from 10 to 1 000 μm , preferably from 10 to 500 μm ,
- the layer based on a liquid coating material has a thickness of from 15 to 200 μm , preferably from 50 to 100 μm , and
- 10 - the layer based on a powder coating material or a powder coating dispersion has a thickness of from 30 to 200 μm , preferably from 50 to 100 μm .

9. A process for producing a coated film as claimed in any of claims 1 to 8, which comprises
15 applying a powder coating material or a powder coating dispersion to the support layer or to the layer based on a liquid coating material, partially sintering the powder coating material or drying the powder coating dispersion, and, if desired, applying a removable film.

20 10. A molding coated with a film as claimed in any of claims 1 to 8.

11. A method of coating moldings, which comprises applying a film as claimed in any of claims 1 to 8 and then crosslinking the layer based on the powder coating
25 material or the powder coating dispersion, the crosslinking taking place preferably by means of heat supply or radiation.

12. The use of a film as claimed in any of claims 1 to 8 to coat moldings, preferably vehicle bodies and domestic appliances.

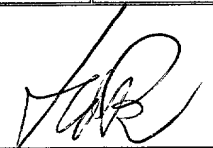


Combined Declaration For Patent Application and Power of Attorney (Continued)		Practitioner's Docket No. IN-5453	
POWER OF ATTORNEY: As a named inventor, I hereby appoint the following attorney(s) and/or agent(s) to prosecute this application and transact all business in the Patent and Trademark Office connected therewith (List name and registration number).			
Anne Gerry Sabourin	Registration No. <u>33,772</u>	Anna M. Budde	Registration No. <u>35,085</u>
Mary E. Golota	Registration No. <u>36,814</u>	Michael P. Brennan	Registration No. <u>30,612</u>
Fernando A. Borrego	Registration No. <u>34,780</u>	Brian Stegman	Registration No. <u>30,977</u>
Karen M. Dellerman	Registration No. <u>33,592</u>	Ryan W. Massey	Registration No. <u>38,543</u>
		Registration No.	
Send Correspondence to:		Direct Telephone Calls to:	
BASF CORPORATION PATENT DEPARTMENT 26701 TELEGRAPH ROAD SOUTHFIELD, MI 48034-2442		(name and telephone number) Anne Gerry Sabourin (248) 948-2021 Fax (248) 948-2093	
		or Mary E. Golota (248) 948-2020 Fax (248) 948-2093	

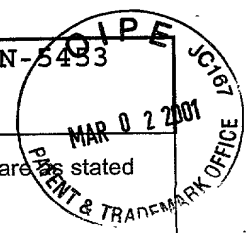
DECLARATION

I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code, and that such willful false statements may jeopardize the validity of the application or any patent issued thereon.

SIGNATURE(S)

FULL NAME OF INVENTOR	FAMILY NAME HINTZE-BRÜNING	FIRST GIVEN NAME Horst	SECOND GIVEN NAME
RESIDENCE & CITIZENSHIP	CITY D-48165 Münster <i>DEX</i>	STATE OR FOREIGN COUNTRY Germany	COUNTRY OF CITIZENSHIP German
POST OFFICE ADDRESS	POST OFFICE ADDRESS Thomas-Mann-Weg 9	CITY D-48165 Münster	STATE & ZIP CODE/COUNTRY Federal Republic of Germany
<div style="display: flex; justify-content: space-between; align-items: center;"><div> SIGNATURE OF INVENTOR 201</div><div>Horst HINTZE-BRÜNING TYPED NAME</div><div><i>12.02.2001</i> DATE</div></div>			

PAT 98131 PCT/US



Combined Declaration For Patent Application and Power of Attorney			Practitioner's Docket No. IN-5493		
<p>As below named inventor, I hereby declare that: My residence, post office address and citizenship are stated below next to my name.</p> <p>I believe I am the original, first and sole inventor (if only name is listed below) or an original, first and joint inventor (if plural names are listed below) of the subject matter which is claimed and for which a patent is sought on the invention entitled: FILM AND THE USE THEREOF FOR COATING SHAPED PARTS</p> <p>The specification of which (check only one item below):</p>					
<input type="checkbox"/> is attached hereto					
<input type="checkbox"/> Was filed as United States Application Serial No. <u>0</u> / <u> </u> on and <u> </u> . Was amended on <u> </u> (if applicable).					
<input checked="" type="checkbox"/> was filed as PCT international application Number <u>PCT/EP 99/05180</u> on <u>21. July 1999</u> and was amended under PCT Article 19 on <u> </u> (if applicable).					
<p>I hereby state that I have reviewed and understand the contents of the above-identified specification, including the claims, as amended by any amendment referred to above.</p> <p>I acknowledge the duty to disclose information which is material to the examination of this application is accordance with Title 37, Code of Federal Regulations, § 1.56(a).</p> <p>I hereby claim foreign priority benefits under Title 35, United States Code § 119 of any foreign application(s) for patent or inventor's certificate of any PCT international application(s) designating at least one country other than the United States of America listed below and have also identified below any foreign application(s) for patent or inventor's certificate or any PCT international application(s) designating a least one country other than the United States of America filed by me on the same subject matter having a filing date before that of the application(s) of which priority is claimed:</p>					
PRIOR FOREIGN/PCT APPLICATION(S) AND ANY PRIORITY CLAIMS UNDER 35 U.S.C. 119:					
COUNTRY	APPLICATION NUMBER	DATE OF FILING DATE/MONTH/YEAR	PRIORITY CLAIMED UNDER 35 UNDER 35 USC § 119		
German	198 35 193.3	04.08.1998	YES		NO
			YES		NO
			YES		NO
			YES		NO
<p>I hereby claim the benefit under Title 35, United States Code, Sec. § 120 of any United States application(s) or PCT international application(s) designating the United States of America that is/are listed below and, insofar as the subject matter of each of the claims of this application is not disclosed in that/those prior application(s) in the manner provided by the first paragraph of Title 35, United States Code, Sec. § 112, I acknowledge the duty to disclose material information as defined in Title 37, Code of Federal Regulations, Sec. § 1.56(a) which occurred between the filing date of the prior application(s) and the national or PCT international filing date of this application:</p>					
PRIOR US APPLICATIONS OR PCT INTERNATIONAL APPLICATION DESIGNATING THE U.S. FOR BENEFIT UNDER 35 USC § 120:					
U.S. APPLICATIONS			STATUS (Check one)		
U.S. APPLICATION NUMBER	U.S. FILING DATE	PATENTED	PENDING	ABANDONED	
PCT APPLICATION DESIGNATING THE U.S.					
PCT APPLICATION NO.	PCT FILING DATE	U.S. SERIAL NUMBERS ASSIGNED (if any)			

T00000-00000000

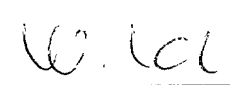
O I P E
MAR 2 2001
PATENT & TRADEMARK OFFICE

Combined Declaration For Patent Application and Power of Attorney (Continued)				Practitioner's Docket No. IN-5453		MAR 2 2001	
POWER OF ATTORNEY: As a named inventor, I hereby appoint the following attorney(s) and/or agent(s) to prosecute this application and transact all business in the Patent and Trademark Office connected therewith (List name and registration number).							
Anne Gerry Sabourin	Registration No.	33,772	Anna M. Budde	Registration No.	35,085		
Mary E. Golota	Registration No.	36,814	Michael P. Brennan	Registration No.	30,612		
Fernando A. Borrego	Registration No.	34,780	Brian Stegman	Registration No.	30,977		
Karen M. Dellerman	Registration No.	33,592	Ryan W. Massey	Registration No.	38,543		
	Registration No.			Registration No.			
Send Correspondence to:		Direct Telephone Calls to:		Direct Telephone Calls to:			
BASF CORPORATION PATENT DEPARTMENT 26701 TELEGRAPH ROAD SOUTHFIELD, MI 48034-2442		(name and telephone number) <u>Anne Gerry Sabourin</u> (248) 948-2021 Fax (248) 948-2093		or (name and telephone number) <u>Mary E. Golota</u> (248) 948-2020 Fax (248) 948-2093			

DECLARATION

I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code, and that such willful false statements may jeopardize the validity of the application or any patent issued thereon.

SIGNATURE(S)

FULL NAME OF INVENTOR	FAMILY NAME <u>LASSMANN</u>	FIRST GIVEN NAME <u>Walter</u>	SECOND GIVEN NAME
RESIDENCE & CITIZENSHIP	CITY <u>D-48165 Münster</u> <i>DEV</i>	STATE OR FOREIGN COUNTRY <u>Germany</u>	COUNTRY OF CITIZENSHIP <u>German</u>
POST OFFICE ADDRESS	POST OFFICE ADDRESS <u>Hülsebrockstr. 32</u>	CITY <u>D-48165 Münster</u>	STATE & ZIP CODE/COUNTRY <u>Federal Republic of Germany</u>
<div style="display: flex; justify-content: space-between; align-items: flex-end;"> <div style="text-align: center;">  SIGNATURE OF INVENTOR 202 </div> <div style="text-align: center;"> <u>Walter LASSMANN</u> TYPED NAME </div> <div style="text-align: center;"> <u>15.02.2001</u> DATE </div> </div>			

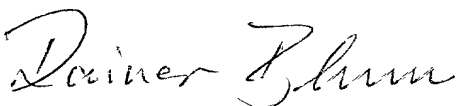


Combined Declaration For Patent Application and Power of Attorney (Continued)				Practitioner's Docket No. IN-5453	
POWER OF ATTORNEY: As a named inventor, I hereby appoint the following attorney(s) and/or agent(s) to prosecute this application and transact all business in the Patent and Trademark Office connected therewith (List name and registration number).					
Anne Gerry Sabourin	Registration No. 33,772	Anna M. Budde	Registration No. 35,085		
Mary E. Golota	Registration No. 36,814	Michael P. Brennan	Registration No. 30,612		
Fernando A. Borrego	Registration No. 34,780	Brian Stegman	Registration No. 30,977		
Karen M. Dellerman	Registration No. 33,592	Ryan W. Massey	Registration No. 38,543		
			Registration No.		
Send Correspondence to:		Direct Telephone Calls to:		Direct Telephone Calls to:	
BASF CORPORATION PATENT DEPARTMENT 26701 TELEGRAPH ROAD SOUTHFIELD, MI 48034-2442		(name and telephone number) <u>Anne Gerry Sabourin</u> (248) 948-2021 Fax (248) 948-2093		or (name and telephone number) <u>Mary E. Golota</u> (248) 948-2020 Fax (248) 948-2093	

DECLARATION

I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code, and that such willful false statements may jeopardize the validity of the application or any patent issued thereon.

SIGNATURE(S)

FULL NAME OF INVENTOR	FAMILY NAME	FIRST GIVEN NAME	SECOND GIVEN NAME
	<u>BLUM</u>	<u>Rainer</u>	
RESIDENCE & CITIZENSHIP	CITY <u>D-67069 Ludwigshafen</u>	STATE OR FOREIGN COUNTRY <u>Germany</u>	COUNTRY OF CITIZENSHIP <u>German</u>
POST OFFICE ADDRESS	POST OFFICE ADDRESS <u>Rüdigerstr. 64</u>	CITY <u>D-67069 Ludwigshafen</u>	STATE & ZIP CODE/COUNTRY <u>Federal Republic of Germany</u>
<div><div>Rainer BLUM</div><div>SIGNATURE OF INVENTOR 203</div></div> <div><div>TYPED NAME</div><div>DATE</div></div>			


MAR 02 2001
 PATENT & TRADEMARK OFFICE

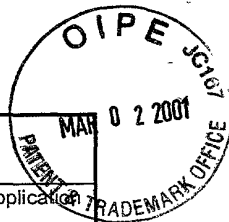
Combined Declaration For Patent Application and Power of Attorney (Continued)				Practitioner's Docket No. IN-5453	
POWER OF ATTORNEY: As a named inventor, I hereby appoint the following attorney(s) and/or agent(s) to prosecute this application and transact all business in the Patent and Trademark Office connected therewith (List name and registration number).					
Anne Gerry Sabourin	Registration No. 33,772	Anna M. Budde	Registration No. 35,085		
Mary E. Golota	Registration No. 36,814	Michael P. Brennan	Registration No. 30,612		
Fernando A. Borrego	Registration No. 34,780	Brian Stegman	Registration No. 30,977		
Karen M. Dellerman	Registration No. 33,592	Ryan W. Massey	Registration No. 38,543		
	Registration No.		Registration No.		
Send Correspondence to:		Direct Telephone Calls to:		Direct Telephone Calls to:	
BASF CORPORATION PATENT DEPARTMENT 26701 TELEGRAPH ROAD SOUTHFIELD, MI 48034-2442		(name and telephone number) <u>Anne Gerry Sabourin</u> (248) 948-2021 Fax (248) 948-2093		or (name and telephone number) <u>Mary E. Golota</u> (248) 948-2020 Fax (248) 948-2093	

DECLARATION

I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that wilful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code, and that such wilful false statements may jeopardize the validity of the application or any patent issued thereon.

SIGNATURE(S)

FULL NAME OF INVENTOR	FAMILY NAME <u>STEGEMANN</u>	FIRST GIVEN NAME <u>Klaus Dieter</u>	SECOND GIVEN NAME
RESIDENCE & CITIZENSHIP	CITY <u>D-48165 Münster</u> <i>DEF</i>	STATE OR FOREIGN COUNTRY <u>Germany</u>	COUNTRY OF CITIZENSHIP <u>German</u>
POST OFFICE ADDRESS	POST OFFICE ADDRESS <u>Wielandstr. 85</u>	CITY <u>D-48165 Münster</u>	STATE & ZIP CODE/COUNTRY <u>Federal Republic of Germany</u>
<div style="display: flex; justify-content: space-between; align-items: flex-end;"> <div>  SIGNATURE OF INVENTOR 204 </div> <div> Klaus Dieter STEGEMANN TYPED NAME </div> <div> <u>15.2.2001</u> DATE </div> </div>			




Combined Declaration For Patent Application and Power of Attorney (Continued)		Practitioner's Docket No. IN-5453	
POWER OF ATTORNEY: As a named inventor, I hereby appoint the following attorney(s) and/or agent(s) to prosecute this application and transact all business in the Patent and Trademark Office connected therewith (List name and registration number).			
Anne Gerry Sabourin	Registration No. 33,772	Anna M. Budde	Registration No. 35,085
Mary E. Golota	Registration No. 36,814	Michael P. Brennan	Registration No. 30,612
Fernando A. Borrego	Registration No. 34,780	Brian Stegman	Registration No. 30,977
Karen M. Dellerman	Registration No. 33,592	Ryan W. Massey	Registration No. 38,543
	Registration No.		Registration No.
Send Correspondence to:		Direct Telephone Calls to:	
BASF CORPORATION PATENT DEPARTMENT 26701 TELEGRAPH ROAD SOUTHFIELD, MI 48034-2442		(name and telephone number) <i>Anne Gerry Sabourin</i> (248) 948-2021 Fax (248) 948-2093	
		or (name and telephone number) <i>Mary E. Golota</i> (248) 948-2020 Fax (248) 948-2093	

DECLARATION

I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code, and that such willful false statements may jeopardize the validity of the application or any patent issued thereon.

SIGNATURE(S)

FULL NAME OF INVENTOR	FAMILY NAME ANTONIETTI	FIRST GIVEN NAME Markus	SECOND GIVEN NAME
RESIDENCE & CITIZENSHIP	CITY D-14558 Bergholz-Rehbrücke	STATE OR FOREIGN COUNTRY Germany	COUNTRY OF CITIZENSHIP German
POST OFFICE ADDRESS	POST OFFICE ADDRESS Am Luchgraben	CITY D-14558 Bergholz-Rehbrücke	STATE & ZIP CODE/COUNTRY Federal Republic of Germany
<div><div>Markus ANTONIETTI <i>Markus Antonietti</i></div><div>13.2.2001</div></div>			
SIGNATURE OF INVENTOR 205		TYPED NAME	DATE